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(54) Title: METALLOCENE PRODUCED POLYETHYLENE FOR FIBRES APPLICATIONS

(57) Abstract: The present invention provides monofilaments or stretched tapes, unwoven or woven into raffia, prepared with metallocene-produced polyethylene having long chain branches.

METALLOCENE PRODUCED POLYETHYLENE FOR FIBRES APPLICATIONS.

5 This invention relates to the field of monofilaments and stretched tapes prepared with metallocene-produced polyethylene.

Monofilaments are uniaxially oriented wire-like polymer strands having a circular cross section. They are manufactured by melt spinning process and their size
10 ranges from 0.1 to 2.5 mm in diameter, depending upon the end use application. Polyethylene, polypropylene, nylon and polyesters are commonly used as raw materials for making monofilaments.

Stretched tapes are prepared from a primary film produced either by a blown or by
15 a cast film process. The film can be cut into tapes and then oriented or reversely, oriented and then cut into tapes. The orientation is carried out by stretching the film or tapes while passing through an air oven or on a hot plate at a temperature below the melting point. The stretching is carried out by passing the film or tapes over two
20 sets of rollers placed respectively before and after the air oven/hot plate and operating at different speeds, the speed of the second set of rollers being larger than that of the first set of rollers.

The polymer preferably used in the market for these applications is a high density polyethylene (HDPE) prepared with a Ziegler-Natta catalyst, said HDPE having a
25 MI2 smaller than 1 g/10min such as for example Solvay Eltex A4009MFN1325 resin or Basell Hostalen GF 7740 F1, GF7740 F2, GF7740 F3, GF7750 M2 grades or the polyethylene resins disclosed in GB-0023662. The molecular weight distribution MWD of these resins is quite broad which means that the resins may include very long as well as very short chains.

30 Semi-crystalline polyethylene (PE) and polypropylene (PP) have also been used as materials for monofilaments stretched tapes and raffia, such as disclosed for example in FR-A-2814761, JP-2001342209 or JP-2001220405. Throughout this

description, raffia is defined as woven monofilaments or woven stretched tapes. The stretched tapes and monofilaments prepared with polyethylene exhibit a higher elongation at rupture, a greater flexibility and a lower tendency to fibrillation than those prepared from polypropylene. These properties are advantageous for
5 example in the production of woven tape fabrics. The products prepared from polyethylene however suffer from the disadvantage their tenacity is much lower than that of the products prepared from polypropylene. Tenacity increases as a function of molecular weight, density, degree of orientation of the chains/crystallites and increases with narrowing of the molecular weight distribution. Impact strength
10 increases with decreasing density, increasing molecular weight and decreasing molecular weight distribution.

There is thus a need for monofilaments or stretched tapes, unwoven or woven into raffia having a better balance of properties.

15 It is an object of the present invention to prepare monofilament or stretched tape products having high tenacity.

It is another object of the present invention to prepare monofilament or stretched
20 tape-products having high impact strength.

It is also an object of the present invention to prepare monofilament or stretched tape products having high elongation at rupture.

25 It is a further object of the present invention to prepare monofilament or stretched tape products having a soft touch.

It is yet another object of the present invention to prepare monofilament or
30 stretched tape products having great flexibility.

Accordingly the present invention provides monofilaments or stretched tapes, unwoven or woven into raffia prepared from metallocene-produced polyethylene (mPE) resin having long chain branches.

- 5 The preferred metallocene catalyst component is based on a terahydroindenyl component or on a constrained geometry component, more preferably on a terahydroindenyl component.

- The invention also provides a process for preparing raffia or stretched tapes with a metallocene-produced polyethylene that comprises the steps of:
- 10 a) providing a metallocene-produced medium density polyethylene resin having long chain branches;
- b) producing a film from the polyethylene resin of step a)
- c) orienting the film obtained from step b) by stretching;
- 15 d) cutting the stretched film of step c) into strips.

Alternatively, the primary film can first be cut into strips and then oriented by stretching.

- 20 The film can be either a blown film or a cast film. Film production is easier with processed material having high melt strength such as polyethylene having long chain branches and/or very long linear chains. Metallocene catalyst systems based on terahydroindenyl components or on constrained geometry components are particularly useful for preparing polyethylene resins having long branches.

- 25 In the production of blown films, the resins prepared with a terahydroindenyl catalyst component provide a very stable bubble thereby leading to films having a uniform thickness and presenting no or very little creases. Uneven thickness and creases are points of weakness when the film is cut into tapes and stretched.

- 30 In the production of cast films, the resins prepared with a terahydroindenyl catalyst component have a stable elongational viscosity leading to a stable and regular thickness.

It is further observed that resins having long branches keep good mechanical properties, such as traction resistance and tenacity, at densities smaller than those of linear resins having equivalent mechanical properties. Working at low densities
5 has the advantage of providing material that has improved flexibility, low fusion temperature and good processability.

Orientation of the primary film or of the cut tapes is carried out by stretching while passing through an air oven or over a hot plate, maintained at a temperature below
10 the melting temperature. Stretching of the primary film or of the cut tapes is done by passing said film or tapes over two sets of rollers (goddet rollers) placed respectively before and after the air oven/hot plate, and operating at different speeds. The stretch ratio $S2/S1$ is defined by the ratio of the speed of roller 2, $S2$ to the speed of roller 1, $S1$ wherein $S2$ is larger than $S1$.

15 Stretching at such high temperature results in chain/crystals orientation with a simultaneous increase of crystallinity. These structural changes lead to an increase of tensile strength and concurrently to a reduction of elongation. The tensile strength increases with increasing stretch ratio and with increasing stretching
20 temperature. It is preferred that the stretching temperature is as close as possible to but smaller than the melting temperature. For high density polyethylene, typical values for the stretch ratio are of from 5.0 to 7.0. The typical stretching temperatures depend upon the melting temperature of the polyethylene resins: they must be lower than but as close as possible to the melting temperature. Typically,
25 they are from 5 to 70 °C lower than the melting temperature of the resin, preferably they are from 10 to 50 °C lower than the melting temperature of the resin.

Preferably, the drawn tapes are annealed immediately after the stretching operation in order to minimise shrinkage that could occur as a result of residual stresses in
30 the oriented tapes. Annealing is done by heating the stretched tapes while they are being transferred from the second goddet rollers onto a third roller having a speed $S3$ that is smaller than the speed of roller 2, $S2$. Preferably, speed $S3$ is about 95 % of speed $S2$. The annealing ratio AR is defined as $(S2-S3)/S2$ at a temperature

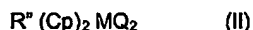
slightly inferior to the stretching temperature. Typically, the annealing temperature is from 5 to 10 °C lower than the stretching temperature.

Polymers that do not include either very long linear chains or long chain branched molecules have a better stretchability. For example, the low density polyethylene (LDPE) having long chain branches cannot be stretched beyond a certain degree, whereas the purely linear polyethylene chains usually obtained with a Ziegler-Natta catalyst have a high degree of stretchability.

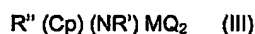
10 The metallocene used to prepare the high density polyethylene can be a bis-indenyl represented by the general formula:



or a bis-cyclopentadienyl represented by the formula



15 or a constrained geometry component of formula



wherein (Ind) is an indenyl or an hydrogenated indenyl, substituted or unsubstituted, Cp is a cyclopentadienyl ring substituted or unsubstituted, R' is hydrogen or a hydrocarbyl having from 1 to 20 carbon atoms, R'' is a structural
20 bridge between the two indenyls to impart stereorigidity that comprises a C₁-C₄ alkylene radical, a dialkyl germanium or silicon or siloxane, or a alkyl phosphine or amine radical, which bridge is substituted or unsubstituted; Q is a hydrocarbyl radical having from 1 to 20 carbon atoms or a halogen, and M is a group IVb transition metal or Vanadium.

25

In formula (I), each indenyl or hydrogenated indenyl compound may be substituted in the same way or differently from one another at one or more positions in the cyclopentadienyl ring, the cyclohexenyl ring and the bridge.

30 In formula (I), each substituent on the indenyl may be independently chosen from those of formula XR_v, in which X is chosen from group IVA, oxygen and nitrogen and each R is the same or different and chosen from hydrogen or hydrocarbyl of from 1 to 20 carbon atoms and v+1 is the valence of X. X is preferably C. If the

cyclopentadienyl ring is substituted, its substituent groups must be so bulky as to affect coordination of the olefin monomer to the metal M. Substituents on the cyclopentadienyl ring preferably have R as hydrogen or CH₃. More preferably, at least one and most preferably both cyclopentadienyl rings are unsubstituted.

5

In a preferred embodiment, both indenyls are unsubstituted and the most preferred catalyst component is a tetrahydroindenyl.

10 In formula (II), each cyclopentadienyl ring may be substituted in the same way or differently from one another at one or more positions in the cyclopentadienyl ring.

15 In formula (II), each substituent on the cyclopentadienyl may be independently chosen from those of formula XR^{*}_v in which X is chosen from group IVA, oxygen and nitrogen and each R^{*} is the same or different and chosen from hydrogen or hydrocarbyl of from 1 to 20 carbon atoms and v+1 is the valence of X. X is preferably C and the most preferred substituent is n-butyl.

20 R^{*} is preferably a C1-C4 alkylene radical (as used herein to describe a difunctional radical, also called alkylidene), most preferably an ethylene bridge (as used herein to describe a difunctional radical, also called ethylidene), which is substituted or unsubstituted.

The metal M is preferably zirconium, hafnium, or titanium, most preferably zirconium.

25

Each Q is the same or different and may be a hydrocarbyl or hydrocarboxy radical having 1 to 20 carbon atoms or a halogen. Suitable hydrocarbyls include aryl, alkyl, alkenyl, alkylaryl or arylalkyl. Each Q is preferably halogen.

30 Among the preferred metallocenes used in the present invention, one can cite bis tetrahydro-indenyl compounds and bis indenyl compounds as disclosed for example in WO 96/35729 or bis(cyclopentadienyl) compounds. The most preferred

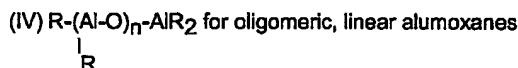
metallocene catalyst is isopropylidene-bis(4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride.

The metallocene may be supported according to any method known in the art. In the event it is supported, the support used in the present invention can be any organic or inorganic solids, particularly porous supports such as talc, inorganic oxides, and resinous support material such as polyolefin. Preferably, the support material is an inorganic oxide in its finely divided form.

The addition on the support, of an agent that reacts with the support and has an ionising action, creates an active site.

Preferably, alumoxane is used to ionise the catalyst during the polymerization procedure, and any alumoxane known in the art is suitable.

The preferred alumoxanes comprise oligomeric linear and/or cyclic alkyl alumoxanes represented by the formula :



And



wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C₁-C₈

alkyl group and preferably methyl.

Methylalumoxane is preferably used.

One or more aluminiumalkyl(s) can be used as cocatalyst in the reactor. The aluminiumalkyl is represented by the formula AlR_x can be used wherein each R is the same or different and is selected from halides or from alkoxy or alkyl groups having from 1 to 12 carbon atoms and x is from 1 to 3. Especially suitable

aluminiumalkyl are trialkylaluminium, the most preferred being triisobutylaluminium (TIBAL).

Further, the catalyst may be prepolymerised prior to introducing it in the reaction zone and/or prior to the stabilization of the reaction conditions in the reactor.

The polyethylene resin of the present invention has a density ranging from 0.925 to 0.950 g/cm³, preferably, from 0.930 to 0.940 g/cm³ and most preferably about 0.935 g/cm³. The melt index MI2 is within the range 0.1 to 5 g/10 min, preferably in the range 0.2 to 1.5 g/10 min.

The density is measured following the method of standard test ASTM D 1505 at 23 °C and the melt index MI2 is measured following the method of standard test ASTM D 1238 at 190 °C and under a load of 2.16 kg.

The metallocene-prepared polyethylenes produce very strong stretched tapes and raffia products, mainly because of their narrow molecular weight distribution and because they have long chain branches. The final products have improved tensile and elongation properties and simultaneously they have improved flexibility and processing properties.

Example.

Several resins have been tested for preparing raffia products.

Resin R1 is a medium density polyethylene resin prepared with isopropylidene (tetrahydroindenyl) zirconium dichloride. It had a density of 0.934 g/cm³ and a melt index MI2 of 0.9 g/10 min. It was additivated as follows:

- 94.5 wt% of resin R1;
- 4 % red masterbatch PE 44930 from Clariant;
- 1 % polymer processing aid AMF 702 from Schuman;
- 0.5 % antibloc masterbatch B1981 from Clariant.

Resin R2 was a commercial resin prepared with a Ziegler-Natta catalyst system: (GF7740 F1 from Hostalen). It had a density of 0.946 g/cm³ and a melt index MI2 of 0.5 g/10min.

- 5 These two resins were treated under the same conditions for blown film production, and for stretching.
- Melt die temperature: 220 °C.
 - Thickness of primary film: 60 microns;
 - Orientation temperature: varied progressively from 80 to 120 °C.
- 10 - Stretch ratio: 7:1

The final products, whether unwoven or woven (nets) obtained from the metallocene-produced resin R1 had a high tenacity, an excellent elongation at rupture and a very high break strength. It also had a soft touch and a high flexibility.

- 15 The properties of the stretched tapes obtained from resins R1 and R2 are summarised in Table I.

TABLE I.

20

	R1	R2
Tenacity at rupture cN/Tex	24.9	22.1
Elongation at rupture %	33.2	29.3
Strength at rupture cN	593	525
Titre Tex	23.8	20.8

The elongation, the strength and the tenacity at rupture of the stretched tapes have been measured following the method of standard test ISO-2062 (1993).

- 25 The titre is measured in tex or g/km: this is a measure of the linear mass of a filament or fibre.

The properties of the woven stretched tapes or raffia are displayed in Table II.

TABLE II.

	R1	R2
Elongation at rupture %	30.6	29.4
Strength at rupture cN	997	811

The raffia products prepared according to the present invention has thus improved
5 properties with respect to those of the prior art.

The elongation and strength at rupture of the raffia have been measured following
the method of standard test ISO-5081 (1977).

CLAIMS.

- 5 1. Monofilaments or stretched tapes, unwoven or woven into raffia prepared from a metallocene-produced polyethylene resin having long chain branches.
2. The monofilaments or stretched tapes of claim 1 wherein the metallocene component is a tetrahydroindenyl.
- 10 3. A process for preparing stretched tapes that comprises the steps of:
- a) providing a metallocene-produced medium density polyethylene resin having long chain branches;
 - b) producing a film from the polyethylene resin of step a)
 - c) orienting the film obtained from step b) by stretching;
 - 15 d) cutting the stretched film of step c) into strips
 - e) optionally, annealing the stretched tapes.
4. The process of claim 4 wherein step d) is performed before step c)
- 20 5. The process of claim 4 or claim 5 wherein the stretching temperature is of from 10 to 70 °C lower than the melting temperature of the resin.
6. The process of claim 6 wherein the stretching temperature is of from 15 to 50 °C lower than the melting temperature of the resin
- 25 7. The process of any one of claims 4 to 7 wherein the ratio of the rollers' velocities is in the range of 5 to 7.
8. The process of any one of claims 4 to 8 wherein the annealing temperature, if annealing is performed, is of from 5 to 10 °C lower than the stretching temperature
- 30

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D01F6/30 D01D5/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D01F D01D C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 12, 29 October 1999 (1999-10-29) -& JP 11 200176 A (HAGIWARA KOGYO KK), 27 July 1999 (1999-07-27) abstract	1,3,4,7
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Y	page 4, line 12 - page 6, line 30 page 11, line 18 - line 25 example 2	3-8
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP2004/050479

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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